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TECHNICAL REPORT

# Template-Directed Crystallization of High Energy Materials

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April 2014

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# REPORT DOCUMENTATION PAGE

*Form Approved*
*OMB No. 0704-0188*

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| 1. REPORT DATE *(DD-MM-YYYY)* | 2. REPORT TYPE | 3. DATES COVERED *(From - To)* |
|---|---|---|
| 00-04-2014 | Technical | April 2014 |

**4. TITLE AND SUBTITLE**

Template-Directed Crystallization of High Energy Materials

**5a. CONTRACT NUMBER**
HDTRA1-08-1-0007

**5b. GRANT NUMBER**

**5c. PROGRAM ELEMENT NUMBER**

**6. AUTHOR(S)**

Jennifer Swift

**5d. PROJECT NUMBER**

**5e. TASK NUMBER**

**5f. WORK UNIT NUMBER**

**7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)**

Georgetown University
Department of Chemistry
37th and O Streeets NW
Washington, DC 20057

**8. PERFORMING ORGANIZATION REPORT NUMBER**

**9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)**

Defense Threat Reduction Agency
8725 John J. Kingman Road STOP 6201
Fort Belvoir, VA 22060
PM/Suhithi Peiris

**10. SPONSOR/MONITOR'S ACRONYM(S)**

DTRA

**11. SPONSOR/MONITOR'S REPORT NUMBER(S)**
DTRA-TR-14-30

**12. DISTRIBUTION / AVAILABILITY STATEMENT**

Approved for public release; distribution is unlimited.

**13. SUPPLEMENTARY NOTES**

**14. ABSTRACT**

The objectives of this grant were to (a) examine the solution crystallization of RDX, HMX and CL-20 from a variety of solvents, withdetailed analysis of their phase, size, and morphology properties; (b) to prepare and fully characterize a library of gold-thiol and siloxane monolayers that can serve as crystal nucleation templates and (c) to assess the growth of RDX, HMX and CL-20 on these templates.

**15. SUBJECT TERMS**

High explosives, crystallization, RDX, CL-20, HMX

| 16. SECURITY CLASSIFICATION OF: | | | 17. LIMITATION OF ABSTRACT | 18. NUMBER OF PAGES | 19a. NAME OF RESPONSIBLE PERSON Suhithi Peiris |
|---|---|---|---|---|---|
| **a. REPORT** | **b. ABSTRACT** | **c. THIS PAGE** | SAR | 16 | **19b. TELEPHONE NUMBER** *(include area code)* |
| Unclassified | Unclassified | Unclassified | | | 703-767-4732 |

**Standard Form 298 (Rev. 8-98)**
Prescribed by ANSI Std. Z39.18

# CONVERSION TABLE

Conversion Factors for U.S. Customary to metric (SI) units of measurement.

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MULTIPLY ─────────────────────►  BY ──────────────────────►  TO GET
TO GET ◄─────────────────────  BY ◄──────────────────────  DIVIDE
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| MULTIPLY / TO GET | BY | TO GET / TO GET |
|---|---|---|
| angstrom | $1.000\ 000 \times E\ {-10}$ | meters (m) |
| atmosphere (normal) | $1.013\ 25\ \times E\ {+2}$ | kilo pascal (kPa) |
| bar | $1.000\ 000 \times E\ {+2}$ | kilo pascal (kPa) |
| barn | $1.000\ 000 \times E\ {-28}$ | $meter^2$ ($m^2$) |
| British thermal unit (thermochemical) | $1.054\ 350 \times E\ {+3}$ | joule (J) |
| calorie (thermochemical) | $4.184\ 000$ | joule (J) |
| cal (thermochemical/$cm^2$) | $4.184\ 000 \times E\ {-2}$ | mega joule/$m^2$ ($MJ/m^2$) |
| curie | $3.700\ 000 \times E\ {+1}$ | *giga bacquerel (GBq) |
| degree (angle) | $1.745\ 329 \times E\ {-2}$ | radian (rad) |
| degree Fahrenheit | $t_k = (t°f + 459.67)/1.8$ | degree kelvin (K) |
| electron volt | $1.602\ 19\ \times E\ {-19}$ | joule (J) |
| erg | $1.000\ 000 \times E\ {-7}$ | joule (J) |
| erg/second | $1.000\ 000 \times E\ {-7}$ | watt (W) |
| foot | $3.048\ 000 \times E\ {-1}$ | meter (m) |
| foot-pound-force | $1.355\ 818$ | joule (J) |
| gallon (U.S. liquid) | $3.785\ 412 \times E\ {-3}$ | $meter^3$ ($m^3$) |
| inch | $2.540\ 000 \times E\ {-2}$ | meter (m) |
| jerk | $1.000\ 000 \times E\ {+9}$ | joule (J) |
| joule/kilogram (J/kg) radiation dose absorbed | $1.000\ 000$ | Gray (Gy) |
| kilotons | $4.183$ | terajoules |
| kip (1000 lbf) | $4.448\ 222 \times E\ {+3}$ | newton (N) |
| kip/$inch^2$ (ksi) | $6.894\ 757 \times E\ {+3}$ | kilo pascal (kPa) |
| ktap | $1.000\ 000 \times E\ {+2}$ | newton-second/$m^2$ ($N-s/m^2$) |
| micron | $1.000\ 000 \times E\ {-6}$ | meter (m) |
| mil | $2.540\ 000 \times E\ {-5}$ | meter (m) |
| mile (international) | $1.609\ 344 \times E\ {+3}$ | meter (m) |
| ounce | $2.834\ 952 \times E\ {-2}$ | kilogram (kg) |
| pound-force (lbs avoirdupois) | $4.448\ 222$ | newton (N) |
| pound-force inch | $1.129\ 848 \times E\ {-1}$ | newton-meter (N-m) |
| pound-force/inch | $1.751\ 268 \times E\ {+2}$ | newton/meter (N/m) |
| pound-force/$foot^2$ | $4.788\ 026 \times E\ {-2}$ | kilo pascal (kPa) |
| pound-force/$inch^2$ (psi) | $6.894\ 757$ | kilo pascal (kPa) |
| pound-mass (lbm avoirdupois) | $4.535\ 924 \times E\ {-1}$ | kilogram (kg) |
| pound-mass-$foot^2$ (moment of inertia) | $4.214\ 011 \times E\ {-2}$ | kilogram-$meter^2$ ($kg-m^2$) |
| pound-mass/$foot^3$ | $1.601\ 846 \times E\ {+1}$ | kilogram-$meter^3$ ($kg/m^3$) |
| rad (radiation dose absorbed) | $1.000\ 000 \times E\ {-2}$ | **Gray (Gy) |
| roentgen | $2.579\ 760 \times E\ {-4}$ | coulomb/kilogram (C/kg) |
| shake | $1.000\ 000 \times E\ {-8}$ | second (s) |
| slug | $1.459\ 390 \times E\ {+1}$ | kilogram (kg) |
| torr (mm Hg, $0°$ C) | $1.333\ 22\ \times E\ {-1}$ | kilo pascal (kPa) |

*The bacquerel (Bq) is the SI unit of radioactivity; 1 Bq = 1 event/s.
**The Gray (GY) is the SI unit of absorbed radiation.

# Template-Directed Crystallization of High Energy Materials

Proposal: P2-06B-0022, Program: HDTRA1-08-1-0007

**Overview:**

The objectives of this grant were to (a) examine the solution crystallization of RDX, HMX and CL-20 from a variety of solvents, with detailed analysis of their phase, size, and morphological properties; (b) to prepare and fully characterize a library of gold-thiol and siloxane monolayers that can serve as crystal nucleation templates and (c) to assess the growth of RDX, HMX and CL-20 on these templates.

To date, the work has resulted in 16 presentations and 2 published manuscripts. At least six additional manuscripts (full papers) are in various stages of completion. They should all be submitted within the next year and will acknowledge DTRA support.

**Accomplishments/New Findings:**

**1.     RDX**

(a)     Slow evaporation growth of α-RDX from conventional solvents and co-solvents

Crystal size and morphology are known to affect the sensitivity of explosive compounds. In formulating plastic bonded explosives (PBX) it is generally more desirable to use isometric or prismatic crystals rather than ones with highly anisotropic shapes (plates or needles) for packing efficiency reasons. However, PBX properties are also affected by the nature of the interactions at the crystal-binder interface. Thus, our first efforts focused on elucidatating how RDX crystal morphologies and sizes are related to the solvent conditions from which it is grown, and to put this in context with previous growth studies.

Calculated morphologies (which do not account for solvent effects) predicted {111}, {200}, {020},{210} and {002} faces, consistent with previous reports. Experimentally, we found that RDX crystals exhibit highly variable morphologies when grown from the same solvent, and also when grown from different solvents. RDX crystals grown from acetone, DMF and cyclohexanone exhibited morphologies generally consistent with previous reports. Much of our efforts focused on examining growth from new solvents (THF, nitromethane, pyridine) as well as binary co-solvent mixtures. The latter were used in an effort to improve the solubility in less polar solvents. A summary of the morphologies, major faces and elongation axes observed appears in Table 1.

**Table 1.** Summary of growth morphology, major faces and prism axis α-RDX grown from new solvent and co-solvent systems.

| Solvent | Morphology | Major Faces {*hkl*} | Elongation Axis | Reference |
|---|---|---|---|---|
| Acetone | Varies | (001), (111) | [010] | This work |
| | Prism | (120) | [001] | Elban *et al.* **1984** |
| | Prism | (102), (-210) | [010] | Elban *et al.* **1984** |
| | Equant (Small) | (001), (111) | [010] | Halfpenny *et al.* **1984** |
| | Prismatic (large) | (210) | [001] | Halfpenny *et al.* **1984** |
| | Tabular (rare) | (001), (210) | [010] | Halfpenny *et al.* **1984** |
| THF | Needle | Varies | [010] | This work |
| | Plate | Varies | [010] | This work |
| Nitromethane | Prism | (001), Varies | Varies | This work |
| Pyridine | Prism | (001), (102), Varies | [010] or [100] | This work |
| DMF | Plate | Varies | Varies | This work |
| | Prism | (001) | [010] or [100] | Galdecki *et al.* **1984** |
| | Prism | (210), (111) | [001] | McDermott *et al.* **1971** |
| Cyclohexanone | Large Plate | (100) or (001) | [010] | This work |
| | Needle | (100) | [010] | ter Horst *et al.* **1999**, van der Heijden *et al.* **2004** |
| | Plate | (001) | [010] | Connick *et al.* **1969** |
| γ-butyrolactone | Prism | (210), (111) | [001] | ter Horst *et al.* **1999, 2001** van der Heijden *et al.* **2004** |
| DP | Prism | (100), (210), (111) | [001] | ter Horst *et al.* **1999,** van der Heijden *et al.* **2004** |
| 2:1 Acetone:Nitrobenzene | Prism | (001), (102), (210), (111), (010) | [100] | This work |
| | Plate | (001), (210) | [010] | |
| 2:1 Acetone:Benzene | Varies | Varies | Varies | This work |
| 2:1 Acetone:Pyridine | Cubic Prism | (010), (111) | [100] | This work |
| | Triangular Prism | Varies | [100] | |
| 2:1 THF:Nitrobenzene | Prism | (102), (010), (210) | [100] | This work |
| 2:1 THF:Cyclohexanone | Prism | Varies | [010] or [001] | This work |

To further analyze qualitative differences in RDX crystals grown from various solvents and co-solvents, a series of X-ray topography (XRT) experiments on whole RDX crystals was performed. Previous XRT work on RDX has employed large single crystals sliced along specific planes in order to quantify the magnitude, density and direction of dislocations. Our XRT work used whole single crystals in an effort to obtain a more wholistic view of the defect density as a function of growth solvent. A few early experiments were performed at Argonne National Lab in collaboration with David Black (Topometrix), using joint beam time awarded to Chad Stoltz (Indian Head), Kyle Ramos and Dan Hooks (LANL). This was a good learning opportunity, however, the decommisionning of the monochromatic beamline at Argonne in early 2009 abruptly ended this line of inquiry. (note: this beamline is scheduled to come back online in late

2013)  We redirected our efforts toward white beam topography experiments at the National Synchrotron Light Source (NSLS) at Brookhaven.  It is worth noting that at the outset it was unclear whether white beam topography would even work on RDX samples, but we have demonstrated unambiguously that it does.  There is still a large amount of analysis that needs to be done on the topography data that was obtained.  This must be done in collaboration with topography experts.  However, we can make some general observations which emphasize the importance of solvent effects.

Comparison of acetone-grown plates and prisms (grown from the same batch) revealed that the former had more homogeneous diffraction.  Darker diffraction bands indicative of grain boundaries were observed in prisms.  Similarly, THF-grown plates and needles (again, grown from the same batch) showed differences in their topography, with needles generally showing fewer defects than the plates.  Overall THF single crystals (both morphologies) had fewer defects than those grown from acetone.  This suggests that while prisms are generally more desirable for PBX formulation, the defect densities of more anisotropic morphologies may offer advantages in terms of defects.  RDX crystals grown from nitromethane, cyclohexanone and DMF showed that the defect structures varied greatly from sample to sample.  DMF-grown crystals consistently showed lattice deformations (as opposed to inhomogeneities due to dislocations or lattice misalignments) which likely reflects solvent inclusion in the crystals.

(b)      Drop-cast evaporative growth on templates - characterization of β-RDX

RDX has five known polymorphic forms, though only the α and β phases are observable at room temperature and pressure.  Many literature reports suggest that the metastable β-RDX polymorph is extremely rare due to the limited number of solvents from which it can be grown and its facile conversion to the more stable α-RDX form.  Our efforts to control polymorphism by directed nucleation at designer surfaces revealed that β-RDX can be consistently obtained from a broad range of solvents (acetone, THF, nitromethane, DMSO) and that crystals grown this way remain stable over extended periods of time up to at least a year.  This has enabled the most detailed analysis of their morphological and thermal properties to date.  Profound differences in the behavior of α-RDX and β-RDX upon exposure to electron beam conditions were also observed.

One μl drops of RDX in acetone, THF, nitromethane and DMSO drop cast onto plain glass and piranha cleaned glass slides resulted in fast evaporation and crystallization.  Identification of α and β crystals by Raman spectroscopy revealed concomitant mixtures of α and β-RDX crystals were obtained from most of the drop cast experiments performed in acetone, THF and nitromethane, while crystallization from DMSO typically yielded exclusively one phase or the other in any given drop.  Solvent choice also affected the morphology of the crystals obtained.

In an effort to further explore concentration effects on the α:β distribution of RDX crystals formed, drop cast crystallization was performed from acetone at three different concentrations (5, 10 and 30 mg/mL).  Raman measurements of 50 separate crystals obtained under each set of conditions showed the overwhelming predominance of β deposits from low concentration drops (5-10 mg/mL), and more α crystals appearing from higher concentration drops (30 mg/mL).  The switch to exclusively α-RDX at higher concentrations was ascribed to the larger number of crystals present coupled with convection currents in the evaporating solution which increase the probability of collisions and conversion to the more stable form.  Other solvents showed similar trends, albeit with slightly different α:β ratios.

Given the simplicity of the drop cast method, we also used it as a means to elucidate some of the thermal and material properties of β-RDX.  RDX samples were prepared by drop cast crystallization from DMSO directly into aluminum DSC pans and subjected to phase analysis by Raman microscopy.  Most samples initially identified as β-RDX exhibited an endothermic

transition starting ~188°C and no subsequent transitions.  Hot stage microscopy experiments confirmed this to be the melting transition.  Samples of α- and β-RDX were also drop cast directly onto carbon grids, and SEM imaging revealed some interesting differences in the interactions of α and β single crystals with electromagnetic radiation.  Focused beam irradiation at 30 kV on the very tip of a β-RDX crystal grown from DMSO resulted in localized "bubbling" which we presume is decomposition.  In contrast, spot irradiation on α-RDX crystals grown from nitromethane at 10 kV led to bubbling over the entire crystal.  In α-RDX the transformation began in multiple spots and propagated throughout the crystal, whereas in the β form, the transformation began with cracking on the surface followed by localized bubbling in one spot on the crystal.  From these observations it seems that the energy dissipation mechanisms in a and b are quite different and the localized effects and higher temperature required to effect decomposition in β, may have some advantages in select applications.

(c)      <u>Oriented growth of α-RDX via slow evaporation on siloxane templates</u>

        The template-directed nucleation of RDX was also examined on Au-S monolayers and siloxane monolayers under slow evaporation conditions.  Our results show that the surface functionality and the growth solvent each play significant roles in determining the crystal morphology, nucleation density and surface orientation.  In general, our efforts to control nucleation on gold-alkanethiol monolayers were not very successful, resulting in very high nucleation densities and large aggregates of crystals on the surface.  Furture growth attempts on arylthiol monolayers which have 2D lattice spacings that are more compatible with RDX may be more successful.  In one (as yet not reproduced) control experiment, we inadvertently grew single crystals of hydroxylammonium sulfate on a bare Au surface in our efforts to grow RDX from nitromethane.  We still do not know if this compound was an impurity in the solvent or the RDX, but this unexpected result suggests a unique method to remove trace amounts of sulfurous impurities from a solution. Future efforts to follow up on this curious result may be pursued time permitting.
        Most of our efforts at template-directed nucleation focused on RDX growth on siloxane surfaces.  In these slow evaporation studies, a greater emphasis is placed on understanding how the chemistry of the monolayer affects the nucleation density (and therefore crystal size), phase and morphology.  RDX crystal growth on siloxane monolayers was attempted on alkyl and haloalky (fluoro, bromo, chloro and iodo), hydrogen bond donor and acceptor silanes (amino, cyano and isocyano) and phenyl derivative silanes (phenyl, pyridine and dinitrophenyl).  Highly oriented crystal growth of α-RDX was generally seen only on siloxane surfaces bearing halogen groups and those capable of protonation.  Detailed studies focused on 3-iodopropyl- (Si-3-I), 3-aminopropyl- (Si-3-NH$_2$) and 2,2-pyridylethyl- (Si-2-Pyr2) siloxanes and 3 different solvents (nitromethane, THF and 2:1 acetone:benzene).
        RDX was crystallized by slow evaporation from nitromethane (15 mg/ml), THF (10 mg/ml) and 2:1 acetone/benzene (10 mg/ml) on Si-3-NH$_2$, Si-2-Pyr2 and Si-3-I in fluorinated glass vials.  In general, crystals grown on templates were smaller than comparable solution grown crystals. Prism-shaped crystals formed from nitromethane within 6-10 days and tended to form clusters.  Needles crystallized from THF in 3-5 days on all SAMs and were of the same morphology as seen for solution grown crystals. RDX crystals grown from 2:1 acetone/benzene on Si-3-NH$_2$, Si-2-Pyr2 and Si-3-I surfaces within 1-2 days appeared to form needles.  Morphologies from nitromethane (prisms) and THF (needles) are the same as in conventional solution growth.  In contrast, the range of morphologies seen in 2:1 acetone:benzene was greatly reduced to just needles when surface-directed growth methods are used.
        Nucleation densities could not be obtained in nitromethane given the clustering observed, however, nucleation densities were systematically analyzed in THF and 2:1 acetone:benzene and

are listed in Table 2. The narrow distribution of crystal sizes correlates with an obvious narrowing of the crystal size distribution, though we have not rigorously attempted to characterize particle sizes in this system.  Although PXRD showed only diffraction lines corresponding to α-RDX, Raman microscopy of crystals grown from nitromethane on glass and Si-3-I showed peaks in the ring-breathing region at 847 cm$^{-1}$ (α-RDX) and 835 cm$^{-1}$.  The latter is consistent with β-RDX (but not HMX, which we considered as a potential impurity).  The Raman data was collected on samples scraped from the siloxane.  Given the mechanical transformation of β to α, we had assumed that scraping/grinding samples would have transformed any trace amounts of β, however, it appears that small amounts of β-phase impurities can survive this treatment.

**Table 2.** Nucleation densities of α-RDX on differently functionalized siloxanes in nitromethane, THF and 2:1 acetone:benzene.

| substrate | nitromethane | THF | 2:1 acetone/benzene |
|---|---|---|---|
| piranha cleaned glass substrates | clusters | clusters | 5 ± 2 |
| Si-2-Pyr2 | clusters | 9 ± 1 | 13 ± 6 |
| Si-3-NH$_2$ | clusters | 28 ± 21 | 3 ± 1 |
| Si-3-I | clusters | 36 ± 21 | 6 ± 1 |

Crystals of RDX grown from nitromethane, THF and 2:1 acetone/benzene on different SAMs were analyzed by oriented PXRD while still attached to the substrates.   Comparison with the calculated powder patterns for α-RDX (refcode: CTMTNA) and β-RDX (refcode: CTMTNA05) enabled identification of the Miller planes aligned at the siloxane/crystal interface. α-RDX has many systematically absent reflections in the 2θ =10 – 20° range including: (110), (101), (011), (201), (120) and (012).  None of these are typically dominant faces in α-RDX single crystals.  Crystals grown from THF on all siloxanes showed a single intense peak at 2θ = 17.92°-18.02° corresponding to the (102) plane.   In contrast, crystals grown from nitromethane on all siloxanes were predominantly oriented on the (002) plane.

In order to compare the degree of preferential orientation generated on the different surfaces, we attempted to quantify the ratios of the intensities for the four most intense peaks (111), (002), (021) and (102) relative to the simulated powder patterns.   For crystals grown from THF, the degree of preferential orientation was 1.5 times on the Si-2-Pyr2 SAM and 1.8 times on the Si-3-I SAM compared to crystal growth on glass substrates (which also show some orientation along (002)). No peaks corresponding to β-RDX appear in any template-directed THF growth experiments.  For crystals grown from nitromethane, the (002) face was three times more intense on the Si-2-Pyr2 SAM, and two times more intense on the Si-3-I SAM compared to glass substrates.  Glass substrates additionally showed a small amount of α-RDX oriented along (111) and (221) as well as β-RDX aligned along (111), (500) and (214).  There was some evidence for small amounts of β-RDX growth on the Si-3-I and Si-2-Pyr2 surfaces, but only α-RDX was seen on Si-3-NH$_2$.

In an effort to establish a correlation between RDX sensitivity and the crystallization process, our studies suggest that defect densities as well as both chemical impurities and phase impurities deserve consideration.

## 2. HMX

(a) Solution growth from various solvents and co-solvents

HMX has four known "polymorphic" forms: α-, β- (the most dense and thermodynamically stable at RT), γ-HMX (technically, a hemihydrate), and δ-HMX (stable above 160°C). Comparison of the intermolecular interactions between these conformational polymorphs using Hirshfeld surfaces provides some insight into their similarities and differences. For all polymorphs of HMX, the largest % of close contacts are seen between H•••O interaction, derived from C-H•••O interactions between neighboring HMX molecules in the lattices. The types of intermolecular interactions are most closely related for the β and γ forms, while the α and δ forms are closely related. This is curious since the α, γ, and δ forms are all similar in conformation (chair-chair with the $NO_2$ groups pointing up) and the β form is different (chair with two $NO_2$ groups pointing up and two pointing down). However, the conformation of the β form means that the molecules can pack closely.

In our experience, HMX is generally more difficult to crystallize than RDX. Slow evaporation growth of HMX at RT was examined from a variety of solvents and the resulting material examined by X-ray powder diffraction (PXRD). Results showed that growth from pyridine and cyclohexanone produced phase pure β-HMX. Growth from THF, acetone and nitromethane yielded concomitant mixtures of β-HMX and α-HMX. Growth from 2:1 acetone:benzene yielded concomitant growth of the β-HMX and γ-HMX forms. Crystals were often twinned. Some of these mixed phases may be due to phase transformations, since a γ to β conversion upon grinding, and a solution-mediated α to β conversion have been previously reported.

BFDH morphology calculations for the four HMX forms were done using Mercury CDS 2.4. All three of the RT forms are predicted to have prismatic morphologies. Unlike RDX, a thorough examination of actual HMX growth morphologies has not been reported. We determined the growth morphologies of crystals grown from both single solvents (acetone, THF and nitromethane) and select co-solvents (2:1 acetone:benzene, 2:1 acetone:nitrobenzene and 2:1 acetone:DMSO). In general, HMX is less soluble than RDX, even in most polar solvents, but binary solvent mixtures help address this issue. A summary of growth morphologies of β-HMX appears in Table 3.

**Table 3.** Summary of growth morphology, major faces, and prism axis for β-HMX grown from single and co-solvent systems.

| Solvent | Morphology | Major Faces {hkl} | Elongation Axis |
|---|---|---|---|
| Acetone | Prism | (0-11), (011), (110), (-101), (-110) | [001] |
| THF | Needle | (011), (0-21) | [100] |
| Nitromethane | Prism<br>Plate | (010), (110)<br>(01-1) | [100] or [001]<br>[100] |
| 2:1 acetone:benzene | Elongated Prism | (011), (110), (-110), (1-10) | [100] |
| 2:1 acetone:nitrobenzene | Prism | (011), (110), (-110), (1-10),<br>(01-1), (0-11), (-101) | [100] |
| 2:1 acetone:DMSO | Prism | Varies, (-1-10) | [001] |

Monochromatic XRT of β-HMX crystals grown from nitromethane suggested that the majority of defects were due to grain boundaries. Comparison of the rocking curves one 2 crystals – a prism and a plate, suggested that the former has a wider mosaic spread and more lattice misordering. This preliminary data indicates shape dependent defect densities, and is similar to our observations on RDX. White beam topography experiments were performed on 5 β-HMX crystals grown from each of several solvents (THF and the three co-solvent mixtures

listed in Table 3) in the hopes that differences in defect densities could be correlated with the growth solvents. Overall, the defect structure for β-HMX was dominated by lattice distortions most likely caused by solvent inclusions in the crystal lattice. This is not entirely surprising given that HMX is known to crystallize in dozens of solvate phases. There was some variation among crystals grown from the same solution as well as variation in crystals from different growth solvents, however, crystals grown from 2:1 acetone:benzene system generally exhibited the most uniform contrast.

(b)    Template directed growth of phase pure β-HMX on siloxane substrates

Crystal growth of HMX on a variety of Au-S and siloxane monolayers using slow evaporation growth methods was performed. As in RDX studies, we generally had greater success with siloxanes. HMX crystal growth was attempted on alkyl and haloalky (fluoro, bromo, chloro and iodo), hydrogen bond donor and acceptor (amino, cyano and isocyano) and aromatic (phenyl, pyridine and dinitrophenyl) siloxane templates. Selective growth of β-HMX was observed on CN, NCO and $NH_3$ terminated surfaces and little growth was observed on surfaces terminated with F, Phenyl, $CH_3$ and others. One important lesson learned from these experiments was that experiments gave significantly different results in fluorinated glass vials, since fluorination suppresses nucleation on the walls of the growth container, resulting in much higher quality crystals on the siloxanes.

Both solvent and template were found to affect the morphology of β-HMX. This was especially true in nitromethane and acetone, where crystals changed from prism to plates depending on the template. The β-HMX phase is usually observed exclusively but in a multiplicity of orientations. The exception to this observation is growth on the Si-3-CN surface, in which the elongated prisms grow nearly perpendicular from the surface with their a-axes emergent. Some of the needle-shaped crystals grew with the needle axis oriented perpendicular to the template (i.e. (1-10) plane parallel to the surface) while other needles appear to have fallen down and rest parallel to the template. Analysis of the (1-10) plane of β-HMX does not offer any clear molecular level reason why this orientation should be preferred.

**3.    CL-20**
(a)    Solution growth from various solvents and cosolvents – phase purity and morphology characterization

There are five known polymorphs of CL-20: α (hydrate), β, γ, ε, and ζ , the first four of which can be obtained under ambient temperature and pressure conditions. The performance and stability of CL-20 can be affected by a number of its crystalline properties including the phase purity of the material, as well as the particle size, morphology and defect density of the individual crystallites. Slow evaporation crystallization in fluorinated glass vials was performed from 16 different single solvent and co-solvent systems and the bulk crystalline material was assessed in terms of its phase purity by powder X-ray diffraction, hot stage microscopy and differential scanning calorimetry. These complementary methods confirmed that a concomitant mixture of polymorphs is typically obtained under most of the solution. Results are summarized in Table 4.

**Table 4.** Summary of growth morphology, major faces, and prism axis for CL-20 grown from single and co-solvent systems.

| Solvent | Morphology | Phase |
|---|---|---|
| Benzene | prisms | ε,α,β (PXRD, DSC, XRD) |
| Toluene | prisms | ε, β   (PXRD, XRD) |
| 1-Propanol | prisms, plates | ε,β,α (PXRD, XRD) |
| 2-Propanol | | ε (PXRD) |
| Nitromethane | clumped prisms | ε, α, β, g (PXRD) |
| Dichloromethane | prisms | ε, β (PXRD) |
| DMF | red gel | α,β (PXRD) |
| 9:1  2-Butanone:Benzene | clumped prisms | ε,α (PXRD,XRD) |
| 3:1  2-Butanone:Benzene | clumped prisms | α, β  (PXRD) |
| 1:1  2-Butanone:Benzene | clumped prisms | ε, α (PXRD) |
| 3:1  2-Butanone:Toluene | large prisms | ε,α (PXRD, XRD) |
| 1:1 2-Butanone: Toluene | large prisms | α,ε (XRD) |
| 3:1  2-Butanone:1-Propanol | prisms, needles | α,ε,β (PXRD,XRD) |
| 3:1  Ethyl acetate:Benzene | rounded prisms | ε,α (PXRD,XRD) |
| 5:4:1 Ethyl acetate:1-Propanol: Benzene | jagged prisms | ε,α,β (PXRD) |

Mixtures of α, β and ε were observed from nitromethane, acetonitrile, acetone and 1-propanol, while typically only ε crystals were obtained from toluene and 2-propanol. Solvents with lower boiling points yielded smaller crystal sizes (presumably from less crystallization time) but had no observable effect on the phase. For binary solvents, one solvent with average CL-20 solubility (benzene, toluene, 1-propanol, 2-propanol) is paired with a solvent of high solubility (ethyl acetate, 2-butanone) in varying compositions. This allowed for more concentrated solutions without the addition of heat. A greater variety of forms (e.g. plates, prisms, needles) are observed in the co-solvent systems relative to the single solvent growth which typically yields prisms.

Morphological characterization of numerous individual crystals was also performed using single crystal X-ray goniometry, and the Miller indices compared against calculated BFDH morphologies. All solutions yielded heterogeneous crystal sizes and 1-propanol exhibited the widest variety of morphologies. BFDH calculations for ε-CL-20 suggested {002}, {011}, {110} and {101} to be important families of surfaces governing crystal morphology. Experimental findings show these families were typically the largest observed for the majority of crystals grown, with (10-1) and (110) often appearing as the large faces seen for ε-plates. Growth in 3:1 1-Propanol:2-Butanone also yielded well-formed β prisms and needles large enough to be isolated for indexing. Examination of the packing interactions via Hirshfeld surface analysis showed great similarities among the different polymorphs, which is presumably a contributing factor in their concomitant crystallization.

(b)     CL-20 growth on siloxane monolayers – phase and particle size control

CL-20 crystallization on siloxane monolayers was performed resulting in two very interesting trends.  Large differences in the nucleation densities were observed, though the trends were solvent dependent.  For example, phenyl and Cl terminated surfaces nucleated 2-6X *fewer* crystals in 1- propanol compared benzene, but $CH_3$ and $NH_2$ terminated surfaces nucleated 2-3X *more* crystals in 1-propanol than benzene.  A nucleation density study performed in benzene revealed only ε growth on multiple siloxanes surfaces.  For any given siloxane, increasing the concentration resulted in increased nucleation density rather than increased crystal size,

suggesting that siloxane-directed nucleation can be used to generate crystalline materials with narrow particle size distributions. Furthermore, the crystals nucleated on these surfaces show strong preferred orientations (much stronger than either RDX or HMX).

Many template/solvent combinations yield exclusively ε in multiple orientations. We have also identified conditions which give phase pure α or β. Analysis of the siloxane/crystal interfaces is ongoing, though the preference for a given set of conditions to yield a metastable phase and/or highly oriented ε may or may not provide clues for the molecular-level origins of the surface-directing effects. Computational modeling efforts would we welcome on this front, and toward that end we are hoping to start a funded collaboration with computational chemists at the University of Missouri who can help on this effort.

**Personnel Supported:**
Jennifer A. Swift, faculty member responsible for overseeing project as a whole
Pranoti Navare PhD (postdoctoral associate, 6/12 - 5/13)
Jessica Urbelis (graduate student, 1/08 - 5/13)
Ilana Goldberg PhD (graduate student, 12/07 - 10/11)
Christina Capacci-Daniel PhD (graduate student, 12/07 - 9/09)
Cameron Mohammadi (undergraduate, 1/12 - 5/13)
Adam Hoy (undergraduate, 10/09 - 12/10)
Brian Fochtman (undergraduate, 9/08 - 1/10)
Lindsey Roeker (undergraduate, 3/08 - 5/10)
Aliza Cruz (undergraduate, 9/08 - 1/09)

**Publications\*:**

Jessica H. Urbelis and **Jennifer A. Swift,** "Solvent Effects on the Growth Morphology and Phase Purity of CL-20," *in preparation*

Pranoti S. Navare, Ilana G. Goldberg and **Jennifer A. Swift**, "Oriented Growth of RDX on 2-D Templates," *in preparation*

Ilana G. Goldberg and **Jennifer A. Swift**, "New Insights into the Metastable β Form of RDX," *Crystal Growth & Design,* 12 (2), 1040–1045 (2012)

Christina Capacci-Daniel, Karen J. Gaskell and Jennifer A. Swift, "Nucleation and Growth of Metastable Polymorphs on Siloxane Monolayer Templates," *Crystal Growth & Design,* 10, 2, 952-962 (2010).

\*A minimum of 5 additional manuscripts acknowledging DTRA support are forthcoming including analysis of our studies on: (1) Solvent effects on the growth morphology of RDX; (2) Solvent effects on phase purity and morphology of HMX; (3) Template-directed growth of HMX on siloxane monolayers, (4) Controlling CL-20 polymorphism and particle size by growth on siloxane monolayer templates; (5) Changes in the surface chemistry of silicate glass upon exposure to different solvents and temperatures.

**Interactions / Transitions:**
(a) Conference participation and invited talks

"Crystallization of Energetic Materials on Monolayer Templates," University of Missouri-Columbia (Columbia, Missouri*) to be given Sep 2013 (rescheduled from Feb 2012 due to weather-related airline cancellation).* (invited lecture)

"Crystallization of Energetic Materials on Monolayer Templates," Los Alamos National Lab (Columbia, Missouri*) to be given Jul 2013 (rescheduled from Feb 2012 due to conflict with awarding of beam time).* (invited lecture)

 "Crystallization of Energetic Materials on Monolayer Templates" *Naval Air Weapons Station China Lake* (China Lake, CA) Dec 2012. (invited lecture)

"Crystallization of RDX on 2D Templates: Surface and Solvent Effects," Pranoti Navare, Ilana G. Goldberg and **Jennifer A. Swift**,  245th *ACS National Meeting* (New Orleans, LA) Apr 2013 (poster).

"Crystallization of CL-20 on Monolayer Surfaces," Jessica Urbelis and **Jennifer A. Swift**, *ACS Midwest Area Regional Meeting* (UMBC, MD) May 2012. (poster)

"RDX Polymorphism Revisited," Ilana G. Goldberg and **Jennifer A. Swift**, *18th International Symposium on Industrial Crystallization (ISIC 18)*, (Zurich, Switzerland) Sept 2011 (poster).

"Crystallization of CL-20 on Monolayer Surfaces," Jessica Urbelis and **Jennifer A. Swift**, *Defense Threat Reduction Agency's Basic Research Program for Countering Weapons of Mass Destruction Technical Review*, (Springfield, VA) Jul 2011. (poster)

"Crystal Growth of HMX on Self-Assembled Monolayer Templates," Ilana Goldberg and **Jennifer A. Swift**, *Defense Threat Reduction Agency's Basic Research Program for Countering Weapons of Mass Destruction Technical Review*, (Springfield, VA) Jul 2011. (poster)

"Polymorphism of the Secondary Explosive RDX Revisited," Ilana G. Goldberg and **Jennifer A. Swift**, *ACA Annual Meeting* (New Orleans, LA) May 2011. (seminar)

"Polymorphism of the Secondary Explosive RDX Revisited," Ilana G. Goldberg and **Jennifer A. Swift**, *ACS Midwest Area Regional Meeting* (College Park, MD) May 2011. (poster)

"Crystallization of the Energetic Materials RDX and HMX: Morphology and Structure Properties," Ilana G. Goldberg and **Jennifer A. Swift**, *Materials Research Society Annual Fall Meeting* (Boston, MA) Nov 2010. (poster)

"RDX Crystallization in Different Environments: Solvent and Template Effects" Ilana G. Goldberg and **Jennifer A. Swift**, *Defense Threat Reduction Agency's Basic Research Program for Countering Weapons of Mass Destruction Technical Review*, (Springfield, VA) Aug 2010. (poster) *(\*Best Poster Award\*)*

"RDX Crystallization in Different Environments: Solvent and Template Effects" Ilana G. Goldberg and **Jennifer A. Swift**, *Gordon Research Conference Energetic Materials*, (Tilton, NH) Jun 2010. (poster)

"Crystal Growth of Polymorphic Energetic Materials Using 2D Self-Assembled Monolayers" <u>Ilana G. Goldberg</u>, David Black and **Jennifer A. Swift**, *238<sup>th</sup> ACS National Meeting*, (Washington, DC) Aug 2009. (poster)

"Directed Crystallization on 2D Monolayer Templates," <u>Ilana G. Goldberg</u>, Lindsey E. Roeker, David Black, and **Jennifer A. Swift,** *ACA Annual Meeting*, (Toronto, Ontario) Jul 2009 (seminar)

"Crystal Growth of Polymorphic Energetic Materials," <u>Ilana G. Goldberg</u> and **Jennifer A. Swift**, *Defense Threat Reduction Agency's Basic Research Program for Countering Weapons of Mass Destruction Technical Review*, (Springfield, VA) Oct 2009. (poster)

"Characterization of Polymorphic Compounds," <u>Ilana G. Goldberg</u> and **Jennifer A. Swift**, *ACA Annual Meeting*, (Knoxville, TN) May 2008. (poster) (***\*Pauling Poster Award\*)***

"Characterization of Polymorphic Compounds," <u>Ilana G. Goldberg</u> and **Jennifer A. Swift**, *GRC Energetic Materials*, (Tilton, NH) Jun 2008. (poster)


(b) Consultative and advisory functions to other labs & agencies & other DoD laboratories

NSF – Proposal reviewer, CHE and DMR divisions

(c) Transitions

   Nothing yet to report

**New discoveries, inventions and patent disclosures**
   In discussions with university lawyers about patenting the phase selective growth of CL20 using our template methods.

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